

Attorney Docket No. P63943USO
Serial No. 09/417,135

carbon atoms, and Y represents a nitro group, a nitroso group, a carbonyl group, a carboxyl group or a cyano group.

75. The solid polymer electrolyte according to claim 73, wherein the metal cation is a cation of a metal selected from Li, Na, K, Rb, Cs, Mg, Ca, Ba, Mn, Fe, Co, Ni, Cu, Zn and Ag.

76. The solid polymer electrolyte according to claim 66, wherein the aprotic organic solvent is an aprotic organic solvent selected from ethers or esters.

77. The solid polymer electrolyte according to claim 66, wherein the polyalkylene glycol is polyethylene glycol or polypropylene glycol.

78. The solid polymer electrolyte according to claim 66, wherein the derivative of the polyalkylene glycol is an ether derivative or an ester derivative.

79. The solid polymer electrolyte according to claim 66, wherein the metal salt of the polyalkylene glycol is selected from the group consisting of a sodium salt of the polyalkylene glycol, a lithium salt of the polyalkylene glycol, and a dialkyl aluminum salt of the polyalkylene glycol.

80. A battery comprising:
a solid polymer electrolyte according to claim 66;
a positive electrode; and
a negative electrode.

REMARKS

Claims 51-80 are presented, hereby, in place of claims 36-50.

Claim 66 corresponds to claim 36, rewritten to expressly recite an implicit feature (limitation) of claim 36, i.e., the repeating units A, B, and C are present in the backbone of the recited "polyether copolymer." Claims 52-65 correspond to claims 37-50, respectively, made dependent on claim 66.

Claim 66 contains the subject matter of original claim 1, rewritten to expressly recite features (limitations) inherent in the claim. Claim 66 recites the repeating units (I') and (II'), depicted at page 4 of the present specification, implicit in the "repeating unit derived from propylene oxide" and "repeating unit derived from ethylene oxide," respectively, recited in original claim 1. Claims 67-80 correspond to claims 37-50, respectively, made dependent on claim 66.

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Applicants wish to thank Examiner Julian A. Mercado for the courteous consideration rendered Applicants' representative during a telephone interview on February 26, 2003. During the interview, the rejections of record and possible claim amendments were discussed.

Applicants also wish to thank the Examiner for returning the From PTO 1449 of the IDS filed August 23, 2001, initialed by the Examiner, as previously requested.

Claims 36-50 were rejected under 35 USC 102(a) or 35 USC 103(a) as allegedly unpatentable based on WO98/07772. As counterpart U.S. Patent 5,968,681 (Miura) of WO98/07772 was relied on by the Examiner, Miura is referred to herein, as well.

Claims 36-50 were rejected under the doctrine of obviousness-type double patenting (hereinafter simply referred to as "double patenting") based on claims 1-28 of Miura and based on claims 1, 3, 9, 11, and 13 of U.S. Patent 6,162,563 (Miura '563).

Reconsideration is requested with respect to the aforesaid rejections under §102(a), §103(a), and double patenting.

For anticipation under § 102 to exist, each and every claim limitation, as arranged in the claim, must be found in a single prior art reference. *Jamesbury Corp. v. Litton Industrial Products, Inc.*, 225 USPQ 253 (Fed. Cir. 1985). The absence from a prior art reference of a single claim limitation negates anticipation. *Kolster Speedsteel A B v. Crucible Inc.*, 230 USPQ 81 (Fed. Cir. 1986). A reference that discloses "substantially the same invention" is not an anticipation. *Jamesbury Corp.* To anticipate the claim, each claim limitation must "*identically appear*" in the reference disclosure. *Gechter v. Davidson*, 43 USPQ2d 1030, 1032 (Fed. Cir. 1997) (*emphasis added*). To be novelty defeating, a reference must put the public in possession of the identical invention claimed. *In re Donahue*, 226 USPQ 619 (Fed. Cir. 1985).

To establish *prima facie* obviousness of a claimed invention, all the claim limitations must be taught or suggested by the prior art. *In re Royka*, 490 F.2d 981, 180 USPQ 580 (CCPA 1974). "All words in a claim must be considered in judging the patentability of that claim against the prior art." *In re Wilson*, 424 F.2d 1382, 1385, 165 USPQ 494, 496 (CCPA 1970). A "ground of rejection is simply inadequate on its face . . . [when] the cited references do not support each limitation of [the] claim." *In re Thrift*, 63 USPQ2d 2002, 2008 (Fed. Cir. 2002). When conducting an

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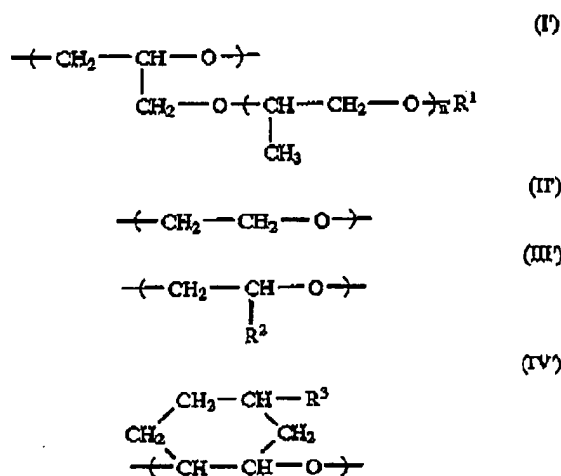
obviousness analysis, "all limitations of a claim must be considered in determining the claimed subject matter as is referred to in 35 U.S.C. 103 and it is error to ignore specific limitations distinguishing over the [prior art] reference." *Ex parte Murphy*, 217 USPQ 479, 481 (PO Bd. App. 1982).

As "[between] *patentably distinct* inventions ... there cannot be [obviousness-type] double patenting." *General Foods Corp. v. Studiengesellschaft Kohle m.b.H.*, 23 USPQ2d 1839, 1843 (Fed. Cir. 1992). "[P]atent claims are looked to only to see what *has been patented*, the subject matter which *has been patented*, not for something one may find to be disclosed by reading them." *In re Aldrich*, 398F.2d 855, 854, 1580 U.S.P.Q. 311, 314 (CCPA 1968)." 23 USPQ2d at 1846.

Copolymerization of EO (ethylene oxide) and PO (propylene oxide), in accordance with the presently claimed invention, gives a copolymer having repeating units of EO and PO in the main (backbone) polymer chain. The repeating units of PO do not form side chains of the polymer.

On the other hand, the polyether copolymer disclosed in Miura does not have repeating units of PO in the main chain. According to Miura (column 3, line 39-column 4, line 2):

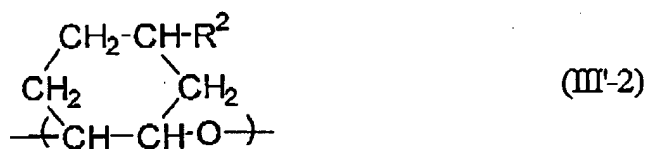
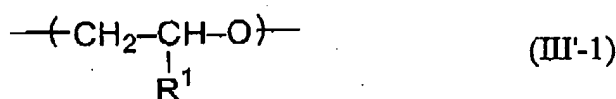
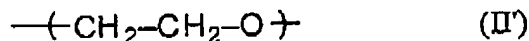
The copolymer prepared by copolymerizing the monomers (I) and (II), and optionally monomer (III) or (IV) has the following repeating units (I') and (II') and optionally (III') or (IV'):



the R² and the R³ in the repeating unit (III') and (IV') are a crosslinkable group.

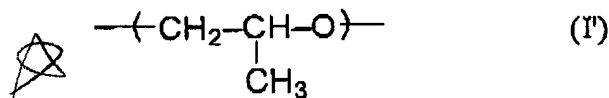
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Repeating units (II'), (III'), and (IV') in Miura appear to correspond to repeating units of (B) and (C) in a sub-genus of the copolymer recited in the present claims, i.e., a copolymer having repeating units of (II'), (III'-1), and (III'-2), respectively (repeating units (II'), (III'-1), and (III'-2) being described at page 4 of the present specification and recited in present claim 66), i.e.,



However, the copolymer in Miura is not disclosed as having any repeating units of (A) - the "repeating units derived from propylene oxide" - in the copolymer recited in the present claims, i.e., the repeating unit

appears
as one of same
unit could group



Miura repeating unit (I') does include a repeating unit derived from propylene oxide; however, it represents part of a *side chain* of the copolymer. The repeating unit derived from propylene oxide is not in the main (backbone) polymer chain.

As such, a limitation on the present claims is absent from Miura and. Accordingly, anticipation of the present claims under §102 based on Miura is negated, *Kolster Speedsteel A B*, *supra*, and the rejection under §102(a) cannot be maintained.

The rejection grounded on Miura for alleged obviousness under §103(a) cannot be maintained for the same reasons as the §102(a) rejection based on the reference cannot be maintained. To establish *prima facie* obviousness of a claimed invention, all the claim limitations must be taught or suggested by the prior art. *Royka, supra*. Since Miura does not support each

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limitation of the present claims, the "ground of rejection is simply inadequate on its face." *Thrift*, 63 USPQ2d at 2008.

Similarly, the double patenting rejection based on *Miura* cannot be maintained. Since the present claims and the claims in *Miura* represent "patentably distinct inventions," one from the other, as explained above, "there cannot be double patenting." *General Foods Corp.*, 23 USPQ2d at 1843.

Moreover, that copolymerization of EO and PO gives the backbone or main chain of the resulting polyether copolymer, i.e., a backbone having repeating units derived from EO and PO, is well known in the art. Submitted, herewith are two documents: *Reports Res. Lab. Asahi Glass Co., Ltd.*, 38, 137-154 (1988) (Document 1), and online *Application Literature*, 18 (14-p1-2) (2001) (URL: http://www.rxeforum.com/FP18-14_page1.htm and http://www.rxeforum.com/FP18-14_page1.htm) (Document 2). Document 1 (page 152) shows various combinations of oxyethylene and oxypropylene units contained in the polymer backbone. For example, Document 1 (page 148) shows -PO-EO-EO- as part of main chain of the copolymer, i.e., both PO and EO are in the main polymer chain. Document 2 (upper drawing in page 1 of 2) discloses the chemical formula of the polyether polyol resulting from a copolymerization reaction, which shows that the polyether polyol has the main chain comprising repeating units derived from EO and PO.

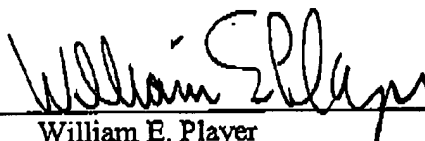
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Favorable action is requested.

Respectfully submitted,

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UDC 543.422.25 : 678.664.03 : 547.42

10. Analysis of Microstructures of EO/PO Polyether Polyols by NMR Measurement*

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and Tadashi Shimada****

The sequential structure of polyether polyols currently used for manufacturing polyurethanes was investigated by ¹⁹F-NMR and ¹³C-NMR.

¹⁹F-NMR measurements were applied to poly ethylene oxide (PEO), poly propylene oxide (PPO), propylene oxide (PO) capped PEO, ethylene oxide (EO) capped EO-PO copolymer. The terminal dyad structures with respect to EO and PO residual sequences and their stereochemical arrangement were identified.

¹³C-NMR measurements were made on PEO, PPO, PO capped PEO, EO capped PPO, EO-PO copolymers and EO capped EO-PO copolymers.

Based on these reference spectra, the 23 signals appeared in the spectra of the polyols were assigned.

The sequential and terminal structures thus elucidated can be related to the physical properties and the reactivity of the polyols.

1 Introduction

Polyether polyols are currently used as the starting materials for manufacturing polyurethanes⁽¹⁾.

The polyols are synthesized by the addition polymerization of alkylene oxides, PO and EO to polyhydroxylic initiators, such as propylene glycol, glycerol, in the presence of KOH as catalyst⁽²⁾.

Usually, the preparation of the polyols starts with the addition polymeriza-

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tion of PO. Resulted PPO's have terminal secondary alcohol groups, whose reactivities toward isocyanates are known to decrease with increasing molecular weight.

To restore the reactivity, EO capping on the terminal PO converts the hydroxyl group into a primary one. This imparts a sufficiently high reactivity to the polyol for the urethane formation.

However, when EO capping is excessive, the resulting polyols have some troubles in exhibiting haze, especially at low temperatures. This is due to the crystallization of the end EO sequences. The occurrence of such haze can be avoided by adopting one of the following synthesis procedures;

- 1) Insertion of PO blocks in the capping EO chains.
- 2) EO capping in the presence of small amounts of PO.
- 3) Preparation of the polyols with EO/PO mixtures.

In any case, the reactivity of the end hydroxyl groups depends on the chemical structure of the chain ends.

The purposes of the present NMR study are twofold.

First, the chemical structures of the terminal and penultimate residues of the EO capped polyols are identified through ^{19}F -NMR measurements of the trifluoroacetic acid (TFA) modified polyols. These polyether polyols are esterified with TFA in CHCl_3 solutions.

Second, the sequence distributions of EO and PO residue in the polyols are characterized by ^{13}C -NMR.

2 Experimental

Samples used for NMR measurements were PEO, PPO, glycerol-initiated PPO's capped with appropriate amounts of EO, glycerol-initiated PEO's capped with appropriate amounts of PO and glycerol-initiated EO-PO copolymers. All the samples were prepared in our laboratory by conventional methods.

Some polyether polyols commercially available for hot moulded foam in Japan were also used for ^{13}C -NMR measurements.

^{19}F -NMR was measured with a JEOL FX-100 FT-NMR at 93.7 MHz for 10 wt% CDCl_3 solutions of the modified polyols.

^{13}C -NMR was measured with the same equipment at 25.05 MHz and also

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with a JEOL FX-200 FT-NMR at 50.14 MHz for 20 wt% $(\text{CD}_3)_2\text{CO}$ solutions of the polymer samples.

3 Results and Discussion

3-1 ^{19}F -NMR measurements of fluorine-modified terminal hydroxyl groups of polyols

The hydroxyl groups were modified by reacting with TFA according to the standard procedure⁽⁹⁾. ^{13}C -NMR measurements of the acetylated samples confirmed quantitative acetylation of the hydroxyl groups by the disappearance of the signals of terminal carbons, $-\dot{\text{C}}\text{H}_2\text{OH}$ and/or $=\dot{\text{C}}\text{OH}$.

^{19}F -NMR spectra of the TFA-modified samples are shown in Fig. 1(a)~(c) and Fig. 2(a), (b). These spectra show well-resolved signals according to the sequence of the terminal and penultimate residues and also according to their stereochemical arrangements.

Figure 1(a) shows the spectrum for TFA-modified PEO which gives a single peak, as expected. Fig. 1(b) shows the spectrum for TFA-modified PPO. The doublet found at -75.73 and -75.77 ppm measured from CFCl_3 is apparently due to the racemic and meso arrangements^{(4),(5),(6)} of the two end residues. Fig. 1(c) shows the spectrum for TFA-modified EO capped PPO, namely $\text{poly}(\text{PO})_n(\text{EO})_m$, where the subscripts are the averaged degree of polymerization. The doublet at the higher field is due to the residual $-\text{POPO}$ and two signals at the lower field are evidently due to $-\text{EOEO}$ and $-\text{POEO}$ from the lower field in order. Fig. 2(a) shows the spectrum for a sample of TFA-modified PO capped PEO, $\text{poly}(\text{EO})_n(\text{PO})_m$.

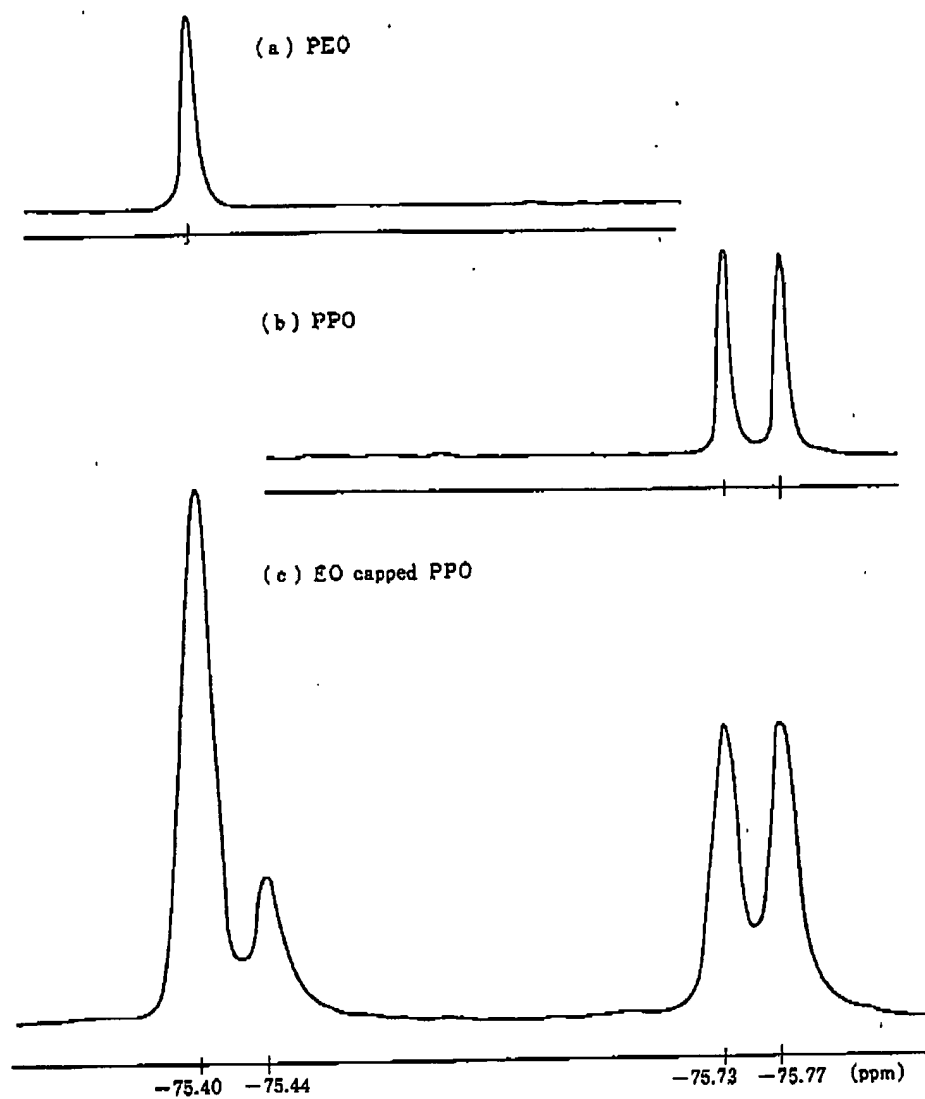
In this case, PEO is not completely masked with PO; the spectrum gives the signals due to the terminal EO and PO.

Figure 2(b) shows the spectrum for another sample of TFA-modified PO capped PEO, $\text{poly}(\text{EO})_n(\text{PO})_m$. By the use of a large excess of PO to PEO, the spectrum shows only the peaks of the end PO; cf, Fig. 1(c).

Figure 2(a) and (b) show three peaks at the region for the terminal PO. Using the changes in the signal intensities, the three signals are assigned to $-\text{EOPO}$ and two $-\text{POPO}$'s respectively, in the order of the field strength.

Thus for EO and PO terminal residues, the amounts of all the possible

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Fig. 1 ^{19}F -NMR spectra of (a) PEO, (b) PPO and (c) EO capped PPO.

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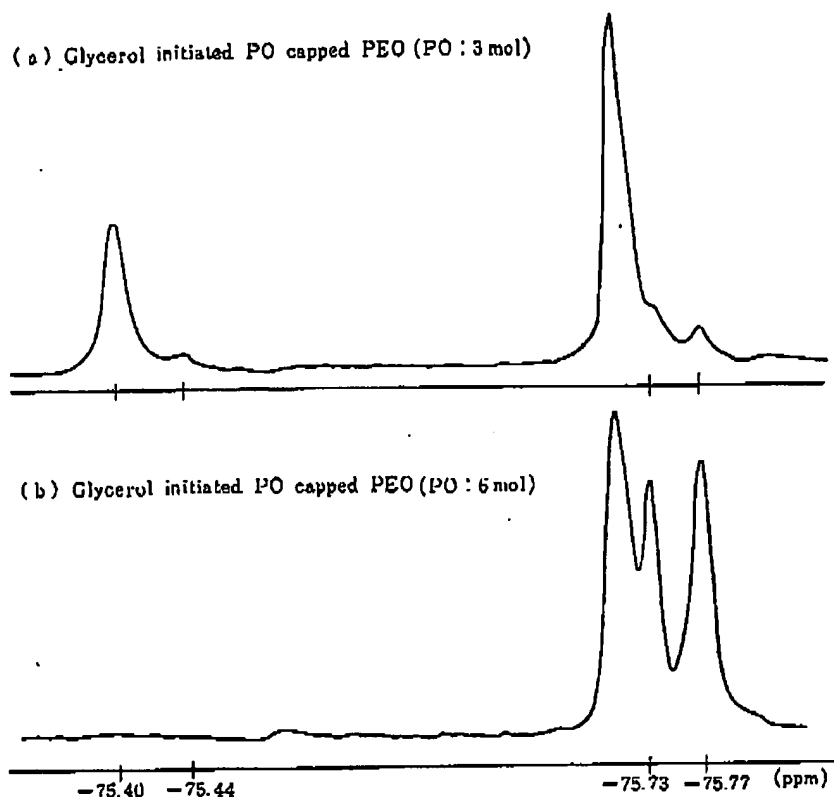


Fig. 2 ^{19}F -NMR spectra of glycerol-initiated PO capped PEO.

arrangements with the penultimate ones, -EOEO, -POEO, -EOPO and -POPO (rasemic and meso), are quantitatively measured by the ^{19}F -NMR measurement of TFA-modified samples.

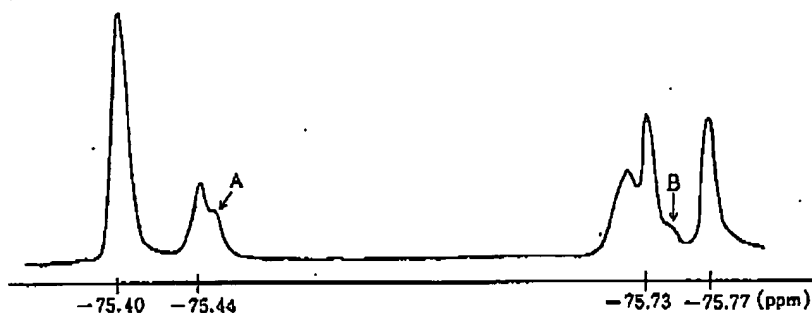
3.2 ^{19}F -NMR spectrum of EO-PO copolymers

Figure 3 shows a typical spectrum for a TFA-modified EO capped EO-PO copolymer. The spectrum apparently shows this polymer has both EO and PO terminal residues. The signals show humps at the position A (-75.45 ppm) and B (-75.77 ppm) where no signals were found in the EO capped PPO [Fig. 1(c)].

These signals can be assigned to those of -EOPOEO(A) and -EOEOPO(B) sequences of the assignments given for Fig. 1(a)~(c) and 2(a), (b). Thus, ^{19}F -NMR for TFA-modified EO-PO copolymer provides the structural information of the end dyad and triad in some detail.

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Glycerol initiated EO capped EO-PO copolymer

Fig. 3 ^{19}F -NMR spectra of EO capped EO-PO copolymer.

3.3 Relationship between the total EO content and the terminal EO content

As mentioned in the Introduction, the reactivity of polyether polyols toward isocyanates depends greatly on the content of the primary hydroxyl groups, or the content of the terminal EO residue.

Based on the signal assignments described above, the molar ratio of the primary hydroxyl groups to the total of the primary and secondary hydroxyl groups was estimated for 17 polyether polyols commercially available in Japan. The ratio is plotted in Fig. 4 against the content of EO in the polymers as defined by the molar ratio of EO residue to the glycerol. The EO content was measured by ^1H -NMR.

The relation shows a saturating trend of the primary hydroxyl content with an increase of the EO content of the polymers. These sample polyols were presumably produced by EO capping.

Therefore, it is presumed that EO capping becomes less effective with added amounts of EO by the well known reactivity difference in the addition EO monomer to the terminal EO and PO residue⁽⁷⁾.

It can also be noticed in this figure that some samples have rather low primary hydroxyl contents as compared to the representative line for the upper most points. Apparently these polyols contain appreciable amounts of EO residue within the chains.

3.4 Relationship between the end EOEO dyad content and the primary hydroxyl content

Figure 5 shows the relationship between the content of the end EOEO

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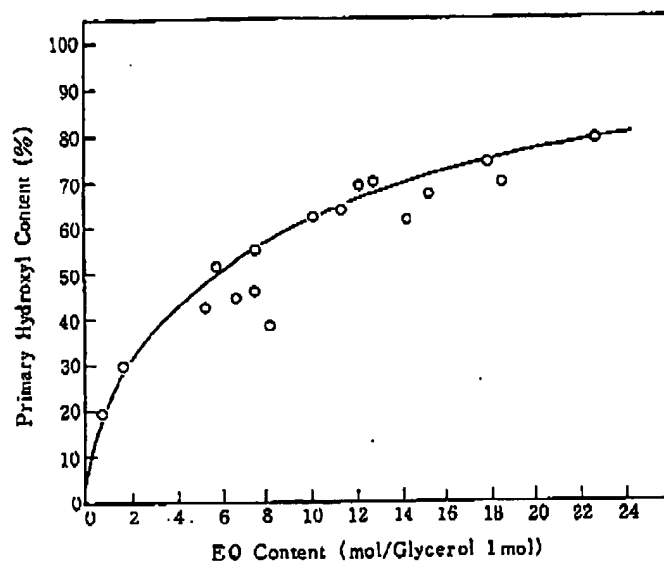


Fig. 4 Relationship between the EO content and primary hydroxyl content with glycerol-initiated polyol.

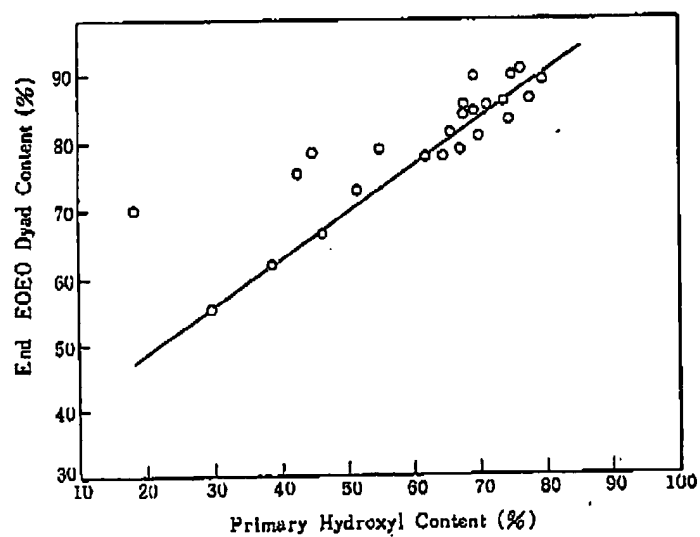


Fig. 5 Relationship between the primary hydroxyl content and EOEO dyad content.

dyad against the primary hydroxyl content for 24 commercially available polyols. Except for several points deviating upwards, the points indicate a linear relation between them. This linear relationship shows that the increase in the end EO is accompanied by an increase in the two EO sequences at the end, which is understood from the above mentioned higher reactivity of EO monomers compared to the EO residue.

However, the points for several samples are seen to deviate substantially from the linear relationship; some samples have unusually high EOEO content. We infer that these samples were prepared either by a special polymerization procedure to the end EO sequence or by the mixing of base polyols with certain amounts of PEO.

Thus, commercially available polyols are presumed to be intentionally modified to meet the user's requirements for the end products.

3.5 Sequential analysis of EO and PO in polyether polyols

It is important to identify the sequential distribution of EO and PO in the polyol chain in relation to the reactivity of polyols to isocyanates and also to the physical properties of the resulting polyurethanes. The analyses were made with ^{13}C -NMR according to the following steps;

3.5.1 ^{13}C -NMR spectrum of PEO

Figure 6 shows the ^{13}C -NMR spectrum of PEO having a MW~1000. In the PEO chain, all the carbon atoms are bonded to oxygen atoms so that carbon signals appear in the range of 60~74 ppm from TMS.

These signals were assigned to the carbons in the EO residue within the chain and to those in the terminal, penultimate and the third residue from the end EO residue.

3.5.2 ^{13}C -NMR spectrum of PPO

Figure 7(a) shows the spectrum of PPO having a MW~2000. The polymer was prepared with KOH as catalyst to give solely a head-to-tail sequence^(*). The signals a (CH_2 ; 18.3 ppm), b (CH_2 ; 74.4 ppm) and c (CH ; 76.2 ppm) were assigned to the PO sequence.

Figure 7(b) shows the expanded spectrum of PPO. This spectrum reveals that the CH_2 and CH signals are composed of two and three peaks corresponding to dyad and triad sequences, respectively, in the chain. Signals with low intensities were found at 67.7 and 66.8 ppm. These were assigned to CH on the terminal residue.

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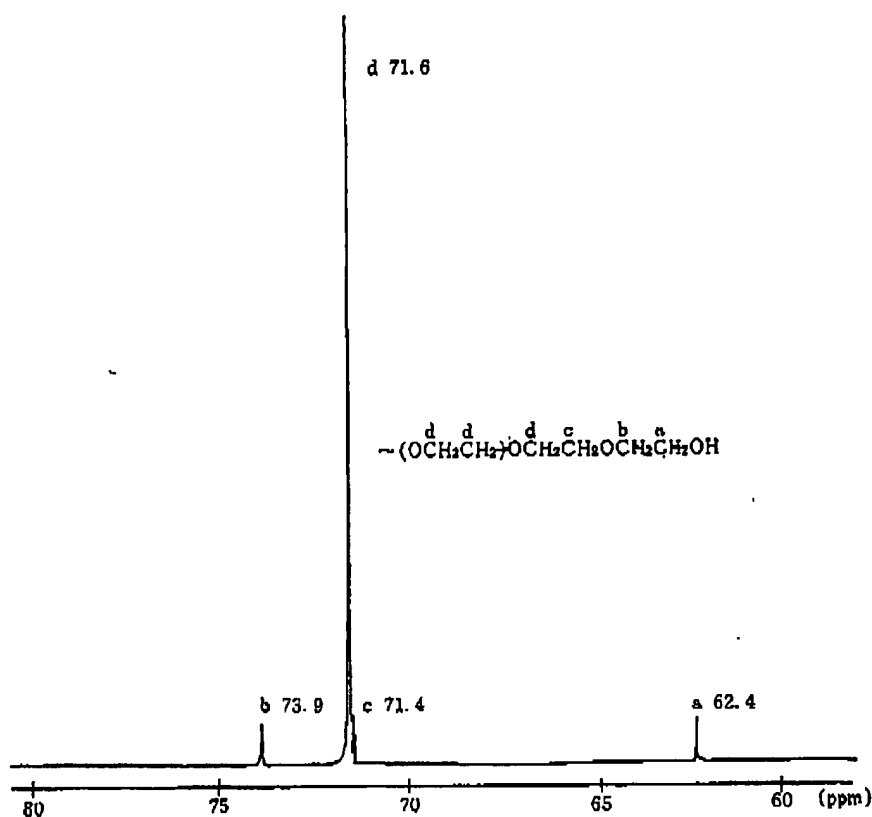


Fig. 6 ^{13}C -NMR spectrum of PEO.

3.5.3 ^{13}C -NMR spectrum of PEO capped with PO

Figure 8(a), (b) and (c) show the ^{13}C -NMR spectra of glycerol-initiated PEO with or without PO capping. Fig. 8(a) shows four peaks in addition to those for PEO shown in Fig. 6.

These signals should be assigned to carbons in glycerol and those in the EO residue adjacent to glycerol. Thus, two peaks at 72.4 and 79.8 ppm were assigned to glycerol CH_2 and CH , respectively and the remaining two peaks at 72.0 and 70.8 ppm assigned to CH_2 's in the EO residue adjacent to glycerol. The latter signal revealed the characteristics for the direct combination of EO to glycerol. PO-capped PEO spectra are shown in Fig. 8(b), (c). These figures show up signals additional to those found in Fig. 8(a), which intensities are increased with the amount of added PO. The peaks at 78.1 and 66.9 ppm in Fig. 8(b) were assigned to CH_2 and CH in the terminal PO attached to EO

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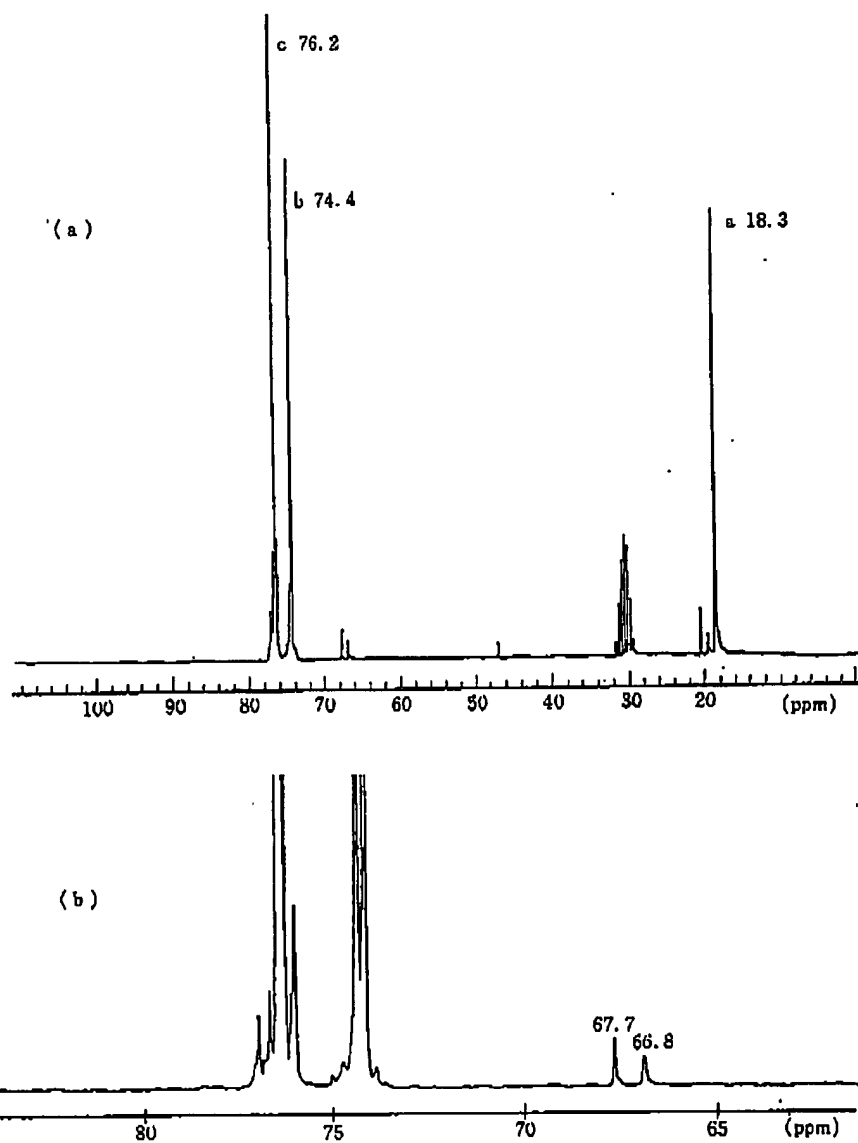


Fig. 7 (a) ^{13}C -NMR spectrum of PFO
(b) The expanded view of methylene and methine carbon region.

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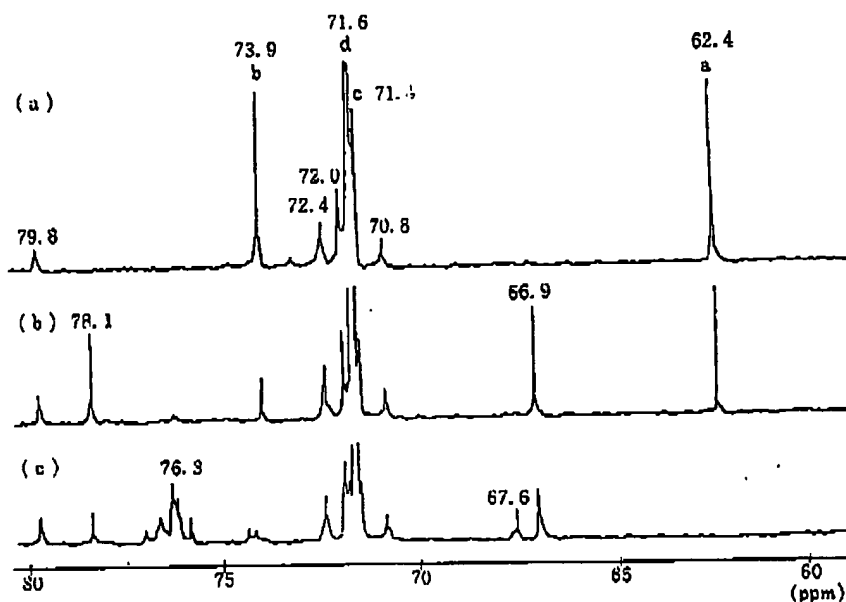


Fig. 8 ^{13}C -NMR spectra of glycerol-initiated PO capped PEO (a) no PO capping (b) 3 moles PO capping (c) 6 moles PO capping.

because of the decreased intensities with an increase of added PO.

The newly appearing signal groups in Fig. 8(c), those at 76.3 and 67.6 ppm were assigned to the stereochemically different CH signals (76.3 ppm) in the PO sequence and to the doublet due to the CH (67.6 ppm) of the terminal PO linked to the penultimate PO. From these figures (a)~(c), it was shown that the terminal EO residue (62.4 ppm) disappeared with the increase of added PO.

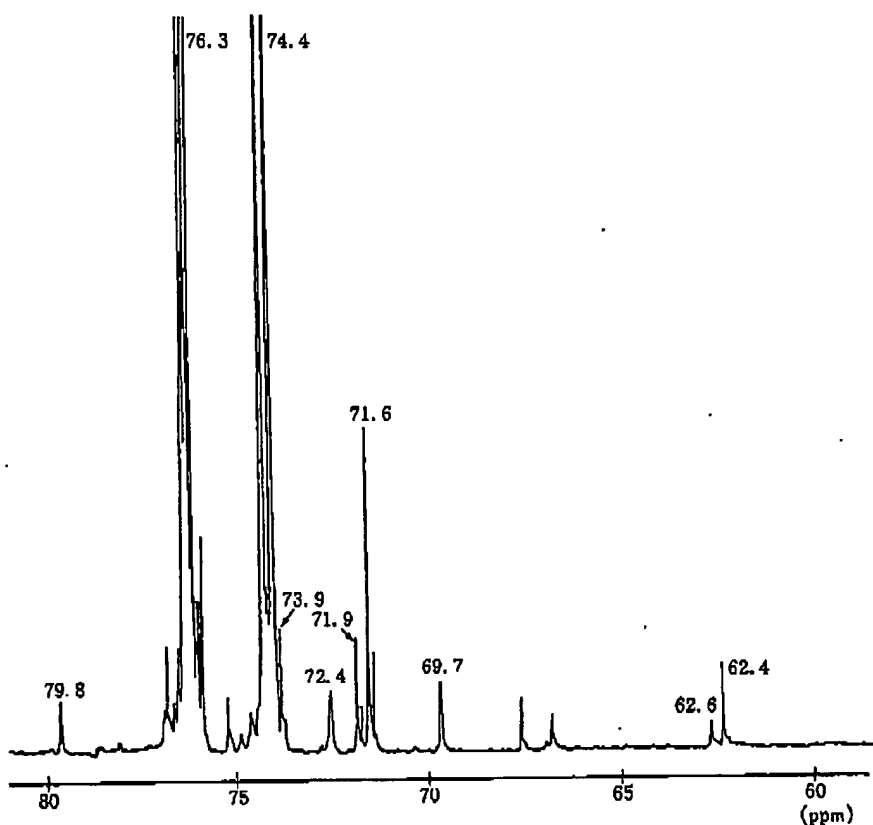
3.5.4 ^{13}C -NMR spectrum of glycerol-initiated EO capped PPO

Figure 9 shows the spectrum of polyol having a MW~3000. Here, the signal groups due to the glycerol and PPO were found as follows;

- a single peak at 79.8 ppm ($\dot{\text{C}}\text{H}_2$ of glycerol)
- signal groups at 76.3 ppm ($\dot{\text{C}}\text{H}_2$ of PPO)
- doublet at 74.4 ppm (CH_2 of PPO)
- a single peak at 72.4 ppm ($\dot{\text{C}}\text{H}_2$ of glycerol)

Additional peak (69.7 ppm) was attributed to the carbons in the EO residue adjacent to PO; these peaks were assigned as follows;

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Fig. 9 ^{13}C -NMR spectrum of glycerol-initiated EO capped PPO.

- a single peak at 73.9 ppm $\left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{-POEO; } \sim\text{OCH}_2\text{COCH}_2\text{CH}_2\text{OH} \\ | \\ \text{H} \end{array} \right)$
- a single peak at 71.9 ppm $\left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{-POEOEO-; } \sim\text{OCH}_2\text{COCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O} \sim \\ | \\ \text{H} \end{array} \right)$
- a single peak at 71.6 ppm $\left(\text{(EO)}_n; \left(\text{OCH}_2\text{CH}_2\text{O} \right)_n \right)$
- a single peak at 69.7 ppm $\left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{-POEO; } \sim\text{OCH}_2\text{COCH}_2\text{CH}_2\text{O} \sim \\ | \\ \text{H} \end{array} \right)$
- double peaks at 62.6 ppm $\left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{-POEO; } \sim\text{OCH}_2\text{COCH}_2\text{CH}_2\text{OH} \\ | \\ \text{H} \end{array} \right)$

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- a single peak at 62.4 ppm ($-\text{EOEO}; \sim\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$)

3.5.5 ^{13}C -NMR spectrum of glycerol-initiated EO-PO copolymers

Figure 10 shows the spectrum of EO-PO copolymer having a MW \sim 3500, prepared with molar ratios of;

$$(\text{EO} + \text{PO})/\text{glycerol} = 37, \text{ and } \text{EO}/\text{PO} = 0.13$$

With the high reactivity of EO monomer, EO residue should be incorporated in the chains and not left at the terminal position. Thus, the spectrum is devoid of the signals of terminal EO, as confirmed by the absence of signals at 62.4 ppm.

Signals for carbons on EO incorporated in the chain appear at 72.1 and

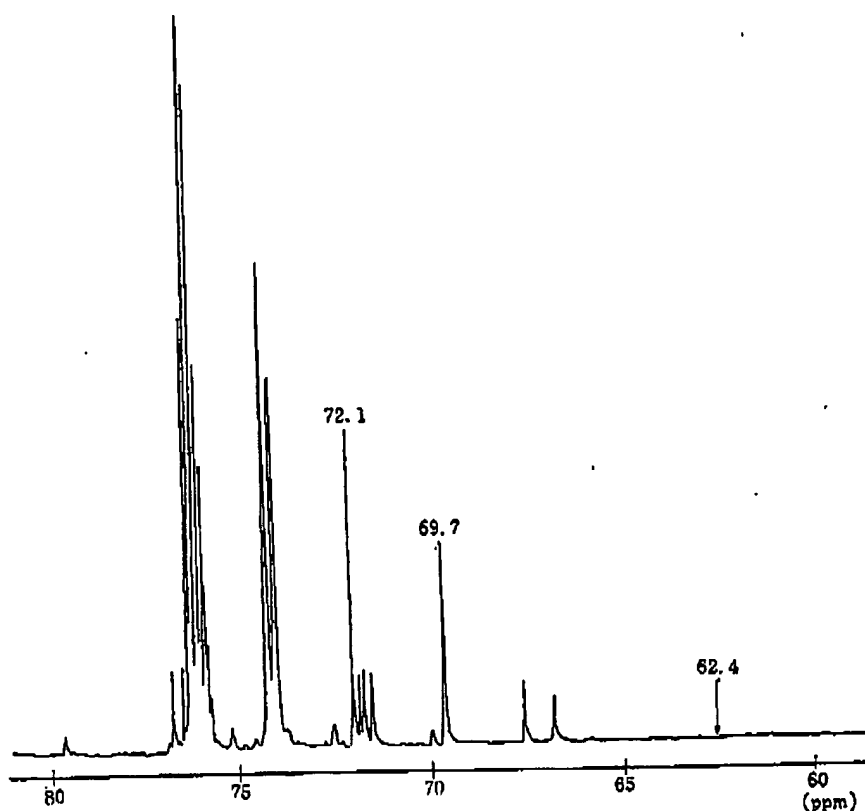


Fig. 10 ^{13}C -NMR spectrum of glycerol-initiated EO-PO copolymer.

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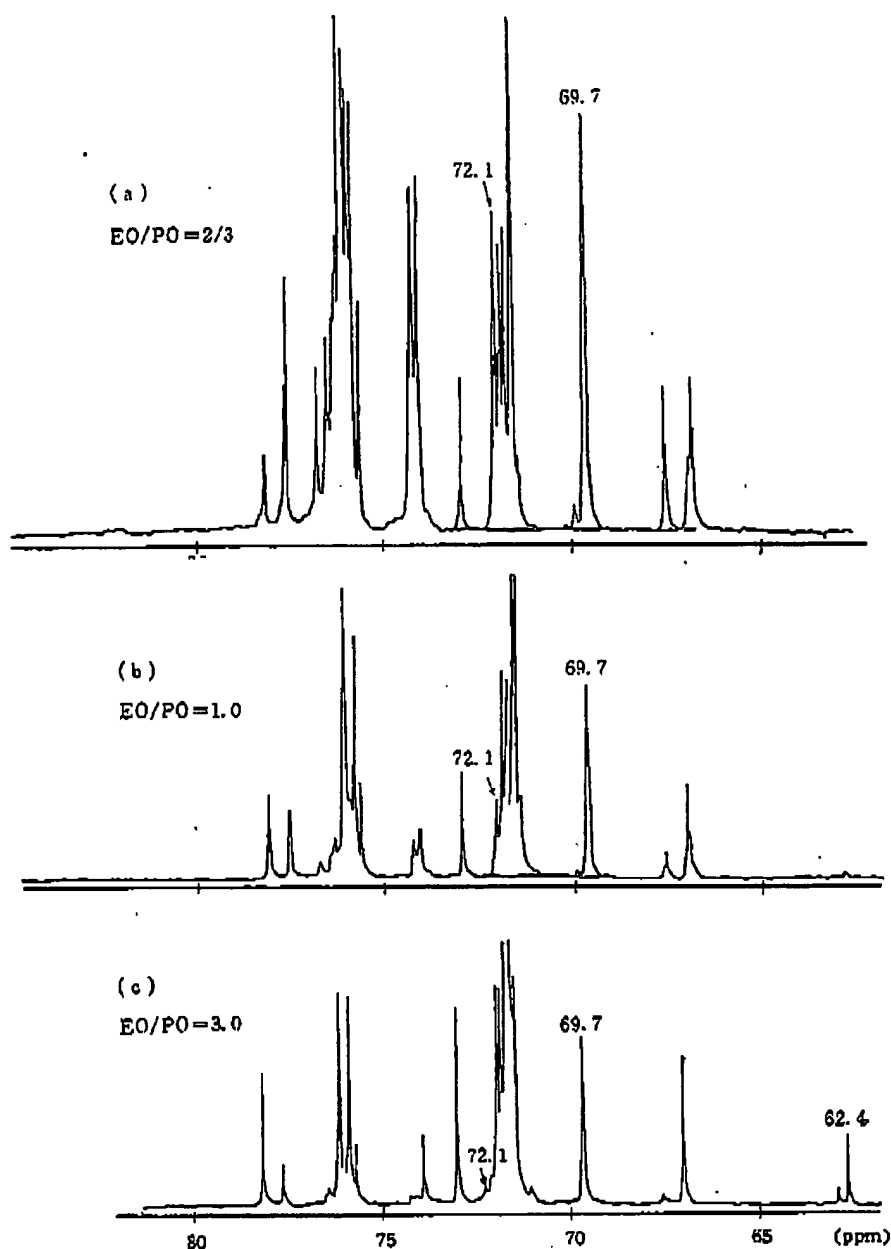


Fig. 11 ^{13}C -NMR spectra of EO-PO copolymer having the different EO/PO ratios.

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69.7 ppm. These are assigned to $\sim\text{POEOPO}$ $\left(\begin{array}{c} \text{CH}_3 \\ | \\ \sim\text{OCH}_2\text{COCH}_2\text{CH}_2\text{OCH}_2\text{CO} \sim \\ | \\ \text{H} \end{array} \right)$ and $\sim\text{POEO}$ $\left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{OCH}_2\text{COCH}_2\text{CH}_2\text{O} \\ | \\ \text{H} \end{array} \right)$ carbons.

3.5.6 Changes in the signal strength with EO/PO ratio in EO-PO copolymers

Figure 11 (a), (b) and (c) show the spectra of the copolymers with EO/PO weight ratio 2/3, 1 and 3, respectively.

With the increase of the EO content, intensities of the signals assigned to EO or PO carbons in certain sequences change as expected.

Figure 12 shown the relationship between the ratio of signal for $\sim\text{POEOPO}$ (72.1 ppm) to that for $\sim\text{POEO}$ (69.7 ppm) and the gross weight ratio of EO to PO residue in the polyols.

EO capped polyols should give points below the representative line. This has been confirmed with capped polyol, which spectrum is shown in Fig. 9.

3.5.7 ^{13}C -NMR spectrum of EO capped EO-PO copolymer

The structural characterization of any commercial polyether polyols can be carried out with the aid of assignments of the signals for the model samples so far described.

In this study, an EO capped EO-PO copolymer were prepared under the

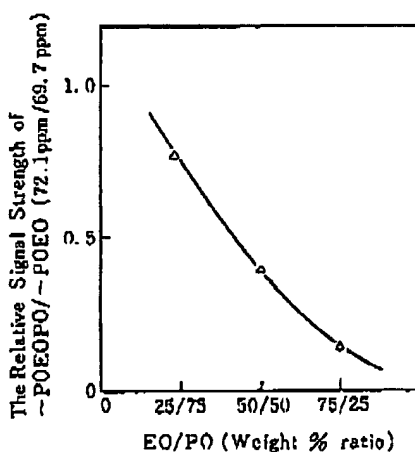


Fig. 12 Relative signal strength of EO/PO ratio in EO-PO copolymer.

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Table 1 The Assignment of ^{13}C -NMR Signals of EO Capped EO-PO Copolymer.

Signal No.	Chemical shift from TMS(ppm)	Sequences
①	62.4	$\sim\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ CH_3
②	62.6	$\sim\text{OCH}_2\text{COCH}_2\text{CH}_2\text{OH}$ H
③	66.7 66.8 67.6	$\sim\text{OCH}_2\text{COCH}_2\text{COH}$ H H CH_3
④	66.9	$\sim\text{OCH}_2\text{CH}_2\text{OCH}_2\text{COH}$ H CH_3
⑤	69.7	$(\text{OCH}_2\text{COCH}_2\text{CH}_2\text{O})_n$ H
⑥	71.5	$\sim\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$
⑦	71.6	$(\text{OCH}_2\text{CH}_2\text{O})_n$
⑧	71.8	$\sim\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$
⑨	71.9	$\sim\text{OCH}_2\text{COCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}\sim$ H CH_3 CH_3
⑩	72.1	$\sim\text{OCH}_2\text{COCH}_2\text{CH}_2\text{OCH}_2\text{CO}\sim$ $\text{CH}_2\text{O}\sim\text{H}$ H CH_3
⑪	72.8	$\text{CHO}\sim$ $\text{CH}_2\text{O}\sim\text{CH}_3$
⑫	73.9	$\sim\text{OCH}_2\text{COCH}_2\text{CH}_2\text{OH}$ H CH_3
⑬ ⑭	74.1 74.3	$(\text{OCH}_2\text{CO})_n$ H CH_3
⑮	75.3	$\text{CH}_2\text{OCH}_2\text{CO}\sim$ $\text{CHO}\sim\text{H}$ CH_2OCH_2
⑯	76.0	$\sim\text{OCH}_2\text{COCH}_2\text{COH}$ H CH_3
⑰ ⑱ ⑲	76.2 76.3 76.4	$(\text{OCH}_2\text{CO})_n$ H CH_3
⑳ ㉑	76.6 76.9	$\sim\text{OCH}_2\text{COCH}_2\text{COH}$ H H CH_3
㉒	78.1	$\sim\text{OCH}_2\text{CH}_2\text{OCH}_2\text{COH}$ $\text{CH}_2\text{O}\sim\text{H}$ CH_3
㉓	79.8	$\text{CHO}\sim$ $\text{CH}_2\text{O}\sim$

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conditions, feed EO/PO molar ratio=1 and capped EO/glycerol=4, was measured by the ^{13}C -NMR measurements.

Figure 13 shows the spectrum. The assignments of all the peaks are summarized in Table 1.

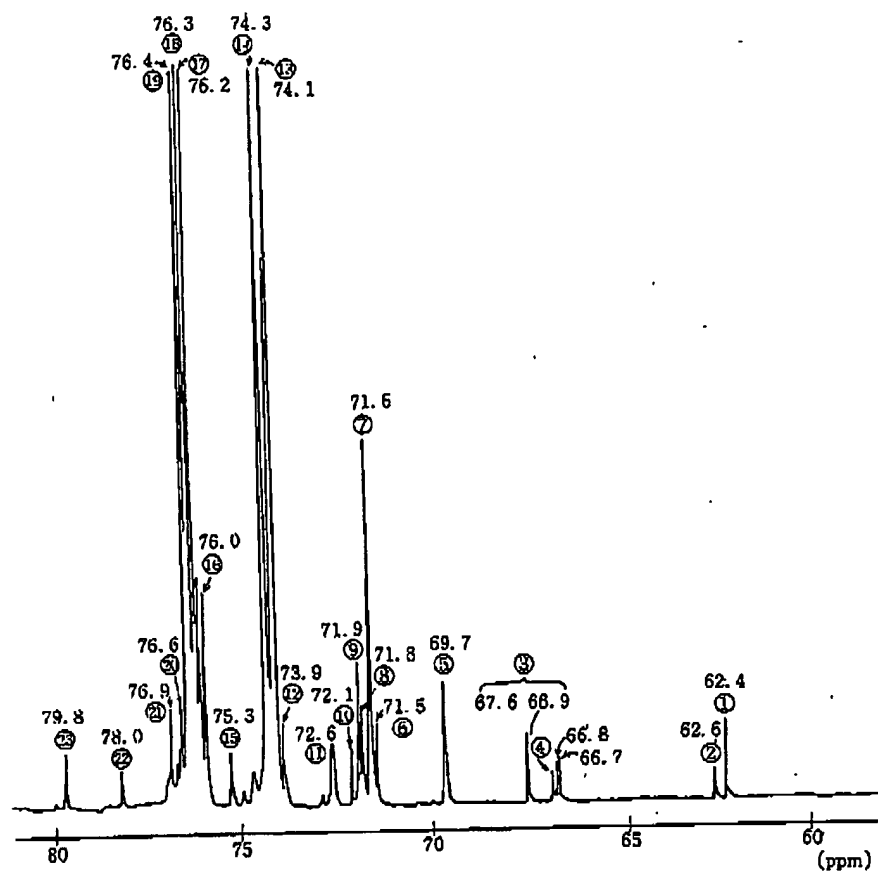


Fig. 13 ^{13}C -NMR spectrum of EO capped glycerol-initiated EO-PO copolymer.
(The expanded view of methylene and methine carbon regions.)

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4 Conclusions

The assignments described so far revealed as a whole the detailed structures of the polyether polyols in several aspects. The initiator glycerol was identified. The monomers adjacent to glycerol, the triad sequences in the chain, and the detailed structures of the dyad or triad at the chain ends were also identified.

Physical properties and the reactivities of the polyether polyols can now be discussed in the light of these clarified structures.

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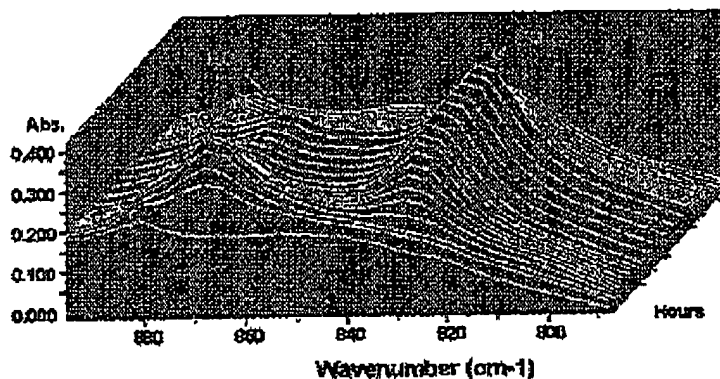
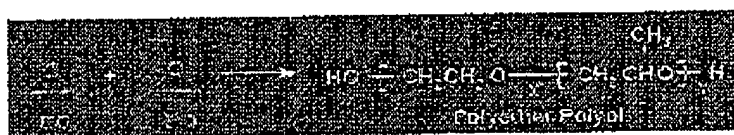
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Other Polymerization

Epoxides can be used to produce a wide range of polyethers, polyols, and glycols. These include copolymers, copolymers and organic intermediates, and final products. Monitoring epoxide monomer consumption rates, product formation rates, and reaction end points is highly valuable in better understanding these processes. These reactions must be monitored in-situ, removing samples would be hazardous and would substantially change the sample (loss of monomer and oxidation of polymer).

In a polyether copolymerization reaction, the ReactIR™ was used to track the levels of ethylene oxide (EO) and propylene oxide (PO) monomers in order to understand their relative rates of uptake. A DiComp™ diamond insertion probe was used in-situ, under conditions of 100°C and 30 psig. Infrared absorbance bands at 869 cm⁻¹ were observed and assigned to C-O-C ring stretching vibrations of the EO and PO monomers, respectively.



Reaction display shows the increase then decrease, of EO at 869 cm⁻¹ and PO at 830 cm⁻¹

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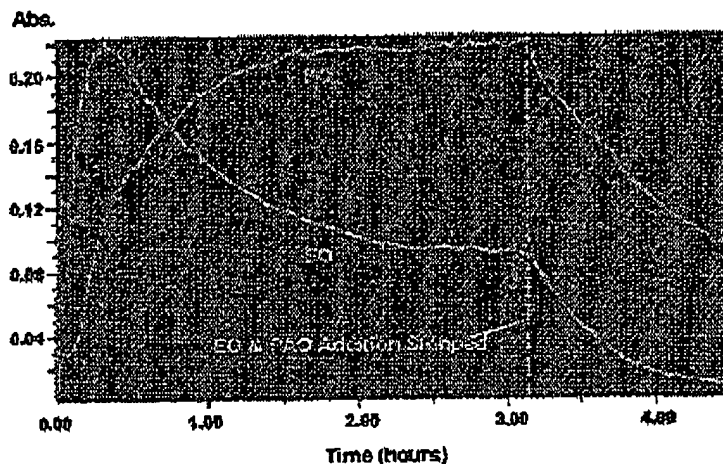
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ether Polymerization)



Absorbance versus Time plot shows changes in concentration of the two monomers as the polymerization proceeds. Clearly the uptake of EO is more rapid than its feed rate, while the PO uptake was slower than its feed rate.

In most polymerizations, little direct information has been available about what occurs in the vessel during reaction. Monomer feed rate is typically measured only to prevent dangerous space pressure. Once monomer feed is complete, the vessel is held for several hours to polymerization. There is no direct measure of when the polymerization is complete.

Monomer concentration levels can now be monitored directly using the ReactIR. In this ether reaction, EO uptake was faster than the feed rate, giving decreasing concentration between 0.5 and 2 hours. PO reacted more slowly in the same time period giving an increase of concentration levels until the feed was stopped. This technique of measuring real rates of monomer uptake provides precise control of final product characteristics.

ReactIR provides a significant amount of information about polymerization reactions. Real-time monomer uptake rates can be precisely monitored and controlled. In addition, molecular structure can be correlated to desired physical properties of the polymer. For example, the degree of cross-linking can be monitored and controlled to optimize the performance of a polymer for a specific application. The extent of reaction completion is simultaneously determined, which is critical in the formation of prepolymers. Polymer reaction completion and any variance can be quickly determined using the ReactIR.

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